Graduate School of Excellence MAINZ

5th MATCOR Student Seminar

Speyer

18.01.2010-20.01.2010

Contents

1 STUDENT TALKS

1.1 Monday, January 18, 2010, time: K. Hild

Energy and angle dependent threshold photoemission magnetic circular dichroism from an ultrathin Co/Pt(111) film

K. Hild[1], G. Schönhense[1], H. J. Elmers[1], T. Nakagawa[2], T. Yokoyama[2] and P. M. Oppeneer[3]

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Threshold photoemission magnetic circular dichroism (TPMCD) has recently been observed in one- and two- photon photoemission (1PPE [1] and 2PPE [2]). We report on measurements for ultrathin Co films with perpendicular magnetization grown on Pt (111) using ultrashort pulse lasers. Energy dependent TPMCD measurements reveal asymmetries, continuously increasing when approaching the photo threshold. At the threshold we obtain maximum values of 1.90% for 1PPE and 12.8% in the case of 2PPE. Angle dependent TPMCD measurements result in reduced asymmetry values for large incident angles following a cosine law in the case of 2PPE. The measured TPMCD asymmetries are compared to theoretical predictions based on local spin density calculations.

Funded by Carl-Zeiss-Stiftung and the Graduate School of Excellence MAINZ (Kerstin Hild) **References:**

[1] T. Nakagawa and T. Yokoyama, Phys. Rev. Lett. 96, 237402 (2006). [2] K. Hild et al., Phys. Rev. Lett. 102, 057207 (2009).

NOTES:

1.2 Monday, January 18, 2010, time: D. Kutnyakhov

Electrophysical and magnetoresistivity properties of granular multilayers based on Co, Ag, Au and Cu

D. Kutnyakhov[1], S. Nepijko[1], I. Cheshko[2], L. Odnodvorets[2], N. Shumekova[2], I. Protsenko[2], and G. Schönhense[1]

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Aiming at a possible use as functional spintronics elements, we study the structural and electrical properties of thin films with spin-depending scattering of electrons based on Co nanoparticles embedded in a matrix of Ag, Au and Cu. Correlations of structure with electrophysical and magnetoresistive properties of these systems are shown, in particular for two- and multilayer films of metastable solid solutions (s.s.) of Ag/Co, Au/Co and Cu/Co. For the systems based on Cu/Co s.s. formed during condensation and partially disintegrated after annealing up to 700 K. For the systems based on Ag/Co or Au/Co s.s. formed during annealing near 700 K, whereas in non-annealed films no s.s. forms. In all systems grains of hcp-Co with 10 nm average size are observed. Formation of s.s. gives rise to change of resistivity, thermal coefficient of resistivity, gauge factor, and magnetoresistance. In the as-grown films no magnetoresistance was observed. After annealing up to 700 K a magnetoresistance of about 0.7% for Ag/Co and 0.4% for Au/Co systems was observed. This change was related with stabilization of granular state of hcp-Co in the matrix.

Project funded by BMBF (UKR 08/022) and by Graduate School of Excellence MAINZ (D.K.)

NOTES:

1.3 Monday, January 18, 2010, time: T. Eichhorn

Free-standing epitaxial films of the magnetic shape memory alloy Ni_2MnGa

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Among the compounds crystallizing in the Heusler structure many systems are of interest due to their predicted high spin polarization making them potential materials for spintronic devices. On the contrary Ni_2MnGa is attracting scientific interest by presenting a ferromagnetic shape memory effect in the low temperature phase (martensite). Moderate magnetic fields can induce large reversible length changes up to 10% in martensitic single crystals. Thereby actuators and sensors with a compact design can be realised using single crystalline thin films of the material. The investigated films are prepared on heated Al_2O_3(11-20) and MgO(100) substrates by dc-magnetron sputtering from alloy targets of different stoichiometry. Samples deposited from a Mn-rich target are martensitic at room temperature and show a modulated orthorhombic structure (7M). The complex crystal structure is studied by x-ray diffraction in 4-circle geometry, whereas magnetic properties are investigated by magnetometry. Since rigid substrates block magnetically induced strains, free-standing films will be needed. One route is to deposit on NaCl(100) substrates that can be easily dissolved in water. The released films are strongly textured, but not single crystalline as desired. Improved crystal quality can be reached by another approach, i.e. introducing a buffer layer on MgO(100) that can be etched selectively.

NOTES:

1.4 Monday, January 18, 2010, time: T. Graf

Structural and Magnetic Properties of the Two Phase Quaternary Heusler Alloy $Co_2Mn_{(1-x)}Ti_xSn$

Tanja Graf[1], Peter Klaer[2], Joachim Barth[1], Christian Blum[1], Benjamin Balke[1], Hans-Joachim Elmers[2], Claudia Felser[1]

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The search for new materials with promising properties for spintronic applications is a field of active research. Heusler compounds are interesting candidates due to their tunable magnetic and structural properties. Here the investigation of the quaternary Heusler alloy $Co_2Mn_(1-x)Ti_xSn$, x=0, 0.2, 0.4, 0.6, 0.8, 1 is presented. The samples were prepared by arc-melting stoichiometric amounts of the concerning elements. The structural properties were determined by powder X-ray diffraction. The materials exhibit the ordered $L2_1$ structure over the whole composition range. Scanning electron microscopy and energy dispersive X-ray spectroscopy analysis of the bulk compounds reveals microstructures that result from phase separation into a Mn-enriched and a Ti-enriched phase. Size, shape and ratio of the microstructures can be altered by varying the composition. The saturation magnetisation and the Curie temperature of the compounds were determined by SQUID magnetometry. The transport properties of the compounds were investigated. A distinct reduction of the thermal lattice conductivity was found due to the microstructure. This makes the phase separation a promising tool to improve the thermoelectric properties of Heusler compounds.

NOTES:

1.5 Tuesday, January 19, 2010, time: L. Mück

“What is the chemical bond?”

Leonie Anna Mück

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The evolvement of chemical bonding models was a milestone in the progress of chemistry as a scientific discipline. A lot of concepts describing bond formation – like the Lewis concept of electron pair bonding – were developed in a purely heuristic manner, but enabled scientists to successfully plan syntheses and explain observations. Especially the Lewis model is handy to use and – although it represents a tremendously simplified description of the molecular electronic structure – seems to be able to capture the relevant parts of the chemical bond in just a few lines.

With the formulation of quantum mechanics in the 1920s chemical bonding models were given a rigorous theoretical foundation. On a quantum chemical basis sophisticated bonding models were developed, a few of which will be presented during the talk. Today these bonding models are widely applied by computational chemists, e. g. in noble gas chemistry.

NOTES:

1.6 Tuesday, January 19, 2010, time: speaker

Confining potentials in the 1D Hubbard model

Stefan Söffing and Sebastian Eggert

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Ultra-cold gases in optical lattices provide an excellent experimental playground to study the Hubbard model in one dimension. While lots of theoretical results are available for periodic or open boundary conditions the effect of trapping potentials is not always clear.

We investigate the low-temperature properties of the Hubbard model with different confinements. The influence of a boundary potential on the density distribution is studied numerically by means of the Density Matrix Renormalization Group (DMRG) calculations and compared to the analytically solvable case of infinitely high potential walls.

Further calculations deal with the situation in optical traps where the confinement is truly harmonic. Exact solutions using Luttinger liquid theory are compared with DMRG calculations at low fillings.

NOTES:

1.7 Tuesday, January 19, 2010, time: D. Muth

Local and non-local relaxation of a 1D Bose gas with finite interactions

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Simulating the dynamics of interacting quantum many-body systems is one of the computationally hardest problems in physics. One of the open questions is, whether integrable models, which have an infinite number of conserved quantities, relax (say, after a quench in the interaction strength) to a state that can be locally fully described by a grand canonical ensemble, defined only by temperature and chemical potential, or whether other quantities have to be taken into account in the Gibbs state. We investigate this question in the case of a 1D Bose gas with repulsive delta-type interactions, as found in recent experiments using ultra-cold gases. Dynamical simulations (employing a matrix-product-states description) of a quench yields both local and non-local correlations. They indicate, that indeed the stationary state for local quantities is identical to the grand canonical one. The same method is applied to the regime of strong attractive interactions. Here experiments have shown, that the system, instead of collapsing into the ground state, remains in a highly excited, metastable state. The properties and process of the formation of this so called super Tonks-Girardeau gas will be explored.

NOTES:

1.8 Tuesday, January 19, 2010, time: Y. Khalavka

One-Sided Growth of Large Plasmonic Gold Domains on CdS Quantum Rods observed on the single particle level

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The synthesis of hybrid nanocrystals composed of domains from different material classes (e.g. magnetic, semiconducting, metal) represents a challenging field in material science. The multiple components of such nano-sized hybrid crystals provide several physical-chemical functionalities within one structure and novel properties are expected via the electronic and electromagnetic coupling between the components. The two most important phenomena arising in nanostructures and altering their electronic and optical properties are quantum confinement in semiconducting nanocrystals (quantum dots) leading to a size tunable band-gap and the electrodynamic confinement in (plasmonic) metal nanocrystals leading to high polarizability at the plasmon frequency. The coupling of plasmons and quantum confinement in metal-semiconductor hybrid systems is poorly understood, mainly due to the difficulty to prepare such systems. Potentially the plasmonic antenna-effect could amplify the excitation or radiative decay of excitons in the semiconductor. Only a few years ago, the controlled crystallographic growth of small gold crystals selectively on the tips of rod-shaped semiconducting nanocrystals emerged, where the metal is in direct crystallographic contact with the semiconductor. Those structures showed a switch from two-sided to one-sided growth attributed to intraparticle electrochemical Oswald ripening. Those dumbbell or matchstick particles were used for directed self-assembly and it was shown that electrons created in the semiconductor by optical excitation transfer and accumulate on the gold tip where they are able to reduce organic molecules. So far, it has not been possible to control the size of the gold domain in those metal-sc hybrids. The gold domains were typically in the order of 1.5-3.5 nm in diameter. Since plasmons in gold nanoparticles are strongly damped for particle diameters below 10-20 nm by surface scattering and the size dependent d-band Fermi-level offset, the poorly understood interaction between plasmons and excitons could not be studied in detail so far. We present a strategy to create large gold domains (up to 15 nm) on CdS or CdSe/CdS quantum rods. The gold domain is large enough to support efficient plasmon oscillations, which leads to a high optical scattering and absorption cross section. The light scattering cross section is large enough to visualize single hybrid particles in a dark-field microscope during the particle growth in real time, which gives new insight into the electrochemical processes involved after photo-excitation of metal-semiconductor hybrid particles. (Nano Lett., Article ASAP, DOI: 10.1021/nl9017918)

NOTES:

1.9 Tuesday, January 19, 2010, time: speaker

Synthesis of Multifunctional Monodisperse MnO Nanocrystals as Potential Hybrid Materials for Biomedical Applications

Schladt, T.D., Schneider, K., Graf, T., Tremel, W.

Johannes Gutenberg Universität, Institut für Anorganische Chemie und Analytische Chemie, Mainz, Deutschland

Magnetic nanoparticles of 3d transition metal oxides have gained enormous interest as new materials for biomedical applications1 such as magnetic separation[2], sensing[3], and as contrast agents for magnetic resonance imaging (MRI)[4]. Although scalable preparative routes to high-quality magnetic nanoparticles are well-established, synthetic routes for surface modification are far less developed, which limits their utility in biological applications. Two common problems are confronted when applying these particles in vivo: their destabilization due to the absorption of plasma proteins and non-specific uptake by reticular-endothelial system (RES), like macrophage cells[5]. Poly(ethylene glycol) (PEG) and PEGylated materials are well-known for their biocompatibility, thus PEGylation of colloidal nanoparticle surfaces has been shown to reduce cytotoxicity and nonspecific protein binding[6]. In this contribution we present single crystalline, highly monodisperse MnO nanoparticles of various sizes, which were synthesized by decomposition of a manganese oleate complex in high boiling non-polar solvents[7]. X-ray powder diffraction (XRD) and transmission electron microscopy (TEM) confirmed phase purity and homogeneity of the particles. Magnetic measurements showed that the magnetic properties strongly depend upon the size of the nanoparticles. Both magnetic moment and blocking temperature increase when the particle size is decreased[7]. The as-prepared MnO nanocrystals were modified by ligand exchange of the oleate groups by novel multifunctional PEGylated polymers. These polymers allow further functionalization of the nanoparticles, e.g. with cell-specific biomolecules. The coated MnO nanocrystals are extremely stable in various aqueous media (e.g. PBS-buffer, human blood serum) and exhibit no cytotoxicity, and high T1 relaxivity coefficients. Therefore, our multifunctional MnO nanoparticles demonstrate strong potential for a variety of bioapplications such optical/magnetic resonance imaging and specific cell targeting.

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[7] Schladt, T. D.; Graf, T.; Tremel, W.; Chem. Mater. 2009, accepted.

NOTES:

1.10 Tuesday, January 19, 2010, time: C. Schade

Wet chemistry route towards nanostructures of thermoelectric antimonides

C. Schade[1], Enrico Mugnaioli[2], Tatiana Gorelik[2], Martin Panthöfer[1], Ute Kolb[2] and Wolfgang Tremel[1]

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[2]*Electron Microscopy Center Mainz, Institute of Physical Chemistry, Johannes Gutenberg - University, Welderweg 11, 55099 Mainz, Germany*

One of the major challenges in thermoelectric research is the design of thermoelectric materials with high figures of merit to open this field to a broader range of applications. One approach to enhance the thermoelectric figure of merit is to create nanostructures, which exhibit low thermal conductivity given by phonon scattering at a large number of interfaces.

We will present a novel solution-based route to a $Zn_{1+x}Sb$ nanophase, containing ZnSb, Zn (which can be removed) and a new binary phase $Zn_{1+\delta}Sb$, segregated from a nano-Zn_4Sb_3 precursor in a peritectoid reaction. The nanoparticular material can be obtained by wet chemistry synthesis under inert conditions from the reaction of activated Zn- and Sb- nanoparticles. The reaction and formation process of the $Zn_{1+x}Sb$ nanoparticles was investigated by time dependent studies. Powder X-ray analysis meets serious problems when the size of the crystals is below 50nm and different phases are present in the sample, all attributes of Zn-Sb systems. Therefore, both phases (ZnSb, $Zn_{1+\delta}Sb$) were

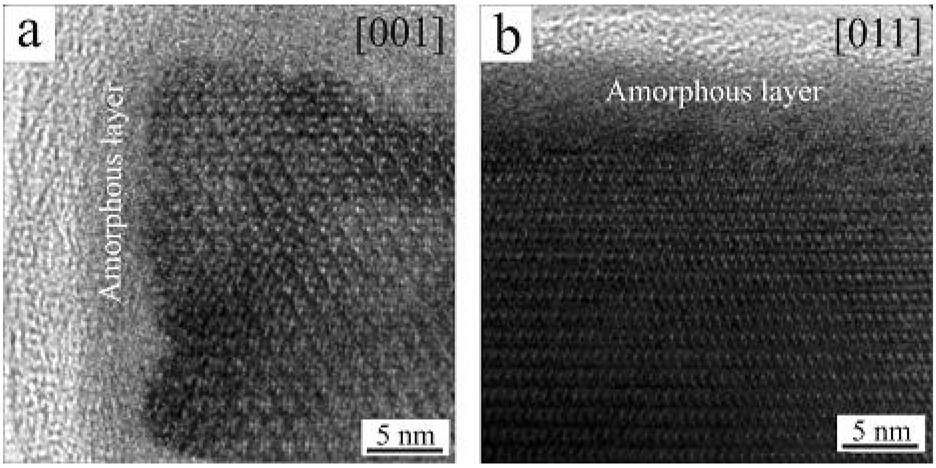

Figure 1: HRTEM images of $Zn_{1+\delta}Sb$ nanoparticles viewed along (a) the [001] and (b) the [011] directions.

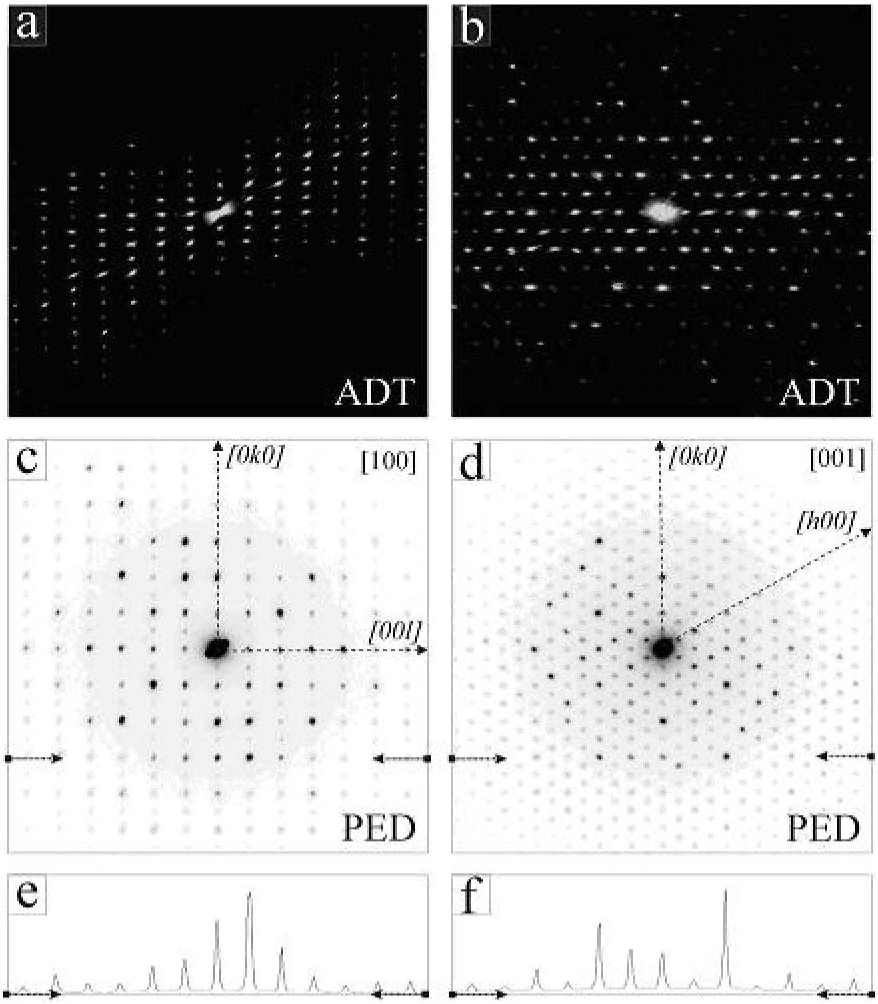

Figure 2: Electron diffraction data for phase II ($Zn_{1+\delta}Sb$): a) projection of the reconstructed reciprocal space along the a* direction; b) projection along the reconstructed reciprocal space along the c* direction; c) single PED pattern zone [100]; d) single pattern zone [001]; e,f) intensity scans of patterns shown in c) and d) (line marked by arrows).

identified by electron diffraction and high-resolution TEM imaging, and *ab initio* structure determinations were performed using combined Automated Diffraction Tomography/Precession Electron Diffraction (ADT/PED). Using a similar synthetic approach, the Fe-Sb system was investigated. Through the reaction of activated Sb-nanoparticles with two different Fe precursors, $FeSb_2$ and FeSb can be obtained depending on the initial stoichiometry and heating rate.

NOTES:

1.11 Wednesday, January 20, 2010, time: S. Rix

A model for long-term damage in CaF_2 for optical applications

Stephan Rix[1,3], Ute Natura[2], Martin Letz[1], Lutz Parthier[2], and Claudia Felser[3]
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[3] *Institute for Inorganic and Analytical Chemistry, Johannes Gutenberg-University, 55099 Mainz, Germany*

Single crystal clacium fluoride (CaF_2) is an important lens material for deep-ultraviolett (DUV) optics, where it is exposed to high radiation densities. The known rapid damage process in CaF_2 cannot account for irreversible damage after long irradiation times. We use densitiy functional methods to calculate the properties of laser-induced defects and to investigate initial stabilization mechanisms on a microscopic level. The mobility of point defects plays an important role in the defect-stabilization mechanisms. Furthermore, experiments indicate the formation of metallic calcium colloids as a result of long-term irradiation.

Single crystal calcium fluoride (CaF_2) is an important lens material in deep-ultraviolet optics, where it is exposed to high radiation densities. Especially for microlithography application extremely high laser stability is required. The rapid damage process in CaF_2 upon ArF laser irradiation has been thoroughly investigated, but cannot account for irreversible damage after long exposure times. We use density functional methods to calculate the properties of laser-induced point defects and to investigate defect stabilization on a microscopic level. We find, that the mobility of point defects plays a major role in the defect stabilization mechanism. While impurities can account for the stabilization of point defects, the agglomeration of F-centers plays a significant role in long-term laser damage of CaF_2. We present a diffusion based model for long-term damage and experimental indications for the formation of metallic Ca colloids after long exposure times of CaF_2 to 193 nm radiation.

NOTES:

1.12 Wednesday, January 20, 2010, time: speaker

Investigation of Cu(In,Ga)Se_2 using Monte Carlo and the Cluster Expansion technique

Christian D. R. Ludwig[1], Thomas Grun[1], Claudia Felser[1] and Johannes Windeln[2]

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CIGS based solar cells are among the most promising thin-film techniques for cheap, yet efficient modules. They have been investigated for many years, but the full potential of CIGS cells has not yet been exhausted and many effects are not understood. For instance, the band gap of the absorber material Cu(In,Ga)Se_2 varies with Ga content. The question why solar cells with high Ga content have low efficiencies, despite the fact that the band gap should have the optimum value, is still unanswered. We are using Monte Carlo simulations in combination with a cluster expansion to investigate the homogeneity of the In-Ga distribution as a possible cause of the low efficiency of cells with high Ga content. The cluster expansion is created by a fit to ab initio electronic structure energies. The results we found are crucial for the processing of solar cells, shed light on structural properties and give hints on how to significantly improve solar cell performance. Above the transition temperature from the separated to the mixed phase, we observe different sizes of the In and Ga domains for a given temperature. The In domains in the Ga-rich compound are smaller and less abundant than the Ga domains in the In-rich compound. This translates into the Ga-rich material being less homogeneous.

NOTES:

1.13 Wednesday, January 20, 2010, time: speaker

Prediction of Insulator to Metal Transition in Rubidium Sesquioxide (Rb_4O_6) under high Pressure

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We show that strongly correlated open-shell 2p Rb_4O_6 exhibits a variety of interesting physical phenomena under high pressure. There are two different kinds of anionic oxygen molecules in the solid simultaneously, hyperoxide and peroxide; the former carry magnetic moments and the latter are strictly non-magnetic at ambient pressure. Around 75 GPa a transition from an insulating antiferromagnetic phase to a half-metallic ferromagnetic phase takes place. The change of the structure is smooth, so that one could assume a second order transition with a quantum critical point. At pressures higher than 75 GPa, all anionic oxygen molecules (peroxide and hyperoxide) carry magnetic moments, yet still possessing a small difference in the bond length. Finally, above 160 GPa a metallic phase appears, where all oxygen molecules possess the same bond length without magnetic moment. We show that the bond length differences of O_2^- and O_2^{--} have a vital effect on magnetism and conductivity of rubidium sesquioxide.

NOTES:

1.14 Wednesday, January 20, 2010, time: K. Medjanik

Searching of the new charge-transfer complexes

Katerina Medjanik and Gerd Schönhense

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The organic molecule tetracyanoquinodimethane (TCNQ) is a strong charge acceptor with a large tendency to form charge transfer compounds. The electronic structure of UHV-deposited mixed phase of the donor tetramethoxypyrene and the acceptor tetracyanoquinodimethane on Au has been studied by UPS. The charge depletion in the donor molecules leads to a shift of the HOMO position to higher binding energies by 0.2eV in the mixed phase in the comparison with the multilayer regime of pure tetramethoxypyrene. A red shift of the CN stretching vibration of TCNQ has been observed in the mixed phase in IR spectroscopy (shift by 7 cm^{-1}). The experimental data were corroborated by DFT calculations.

Project funded via transregio SFB TR49 and Graduate School of Excellence MAINZ.

NOTES:

1.15 Wednesday, January 20, 2010, time: A. Pütz

New stable radicals with a phosphate substituent

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Nitronyl-nitroxide radicals (NIT) are a class of stable radicals. They can be used as spin labels or markers to get an insight in dynamic processes e.g. in polymers or in proteins. But even more important is the combination of NIT radicals with paramagnetic metal ions in the so called “metal-radical-approach”. The resulting new molecular magnetic materials possess higher spin ground states compared to complexes built of diamagnetic ligands. Here we present the synthesis and characterization of two new NIT radicals with an additional phosphonate group (PO_3^{2-}). Their coordination chemistry is investigated by X-ray and SQUID measurements, EPR and other spectroscopic methods.

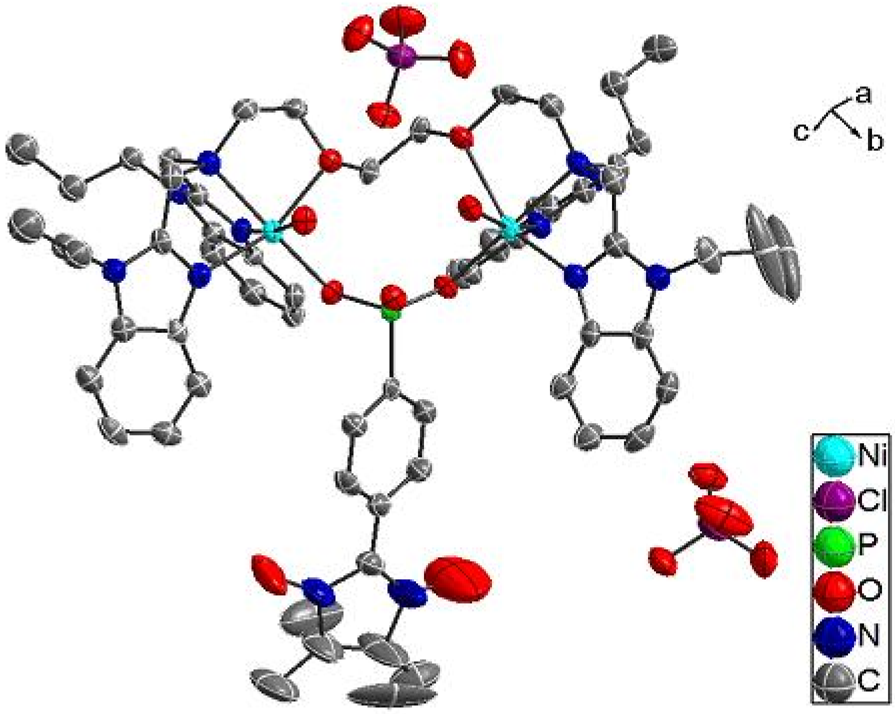

Figure 3: Part of the crystal structure of $[Ni_2(C_{50}H_{64}N_{10}O_2)(C_{13}H_{16}N_2PO_5)(H_2O)_2](ClO_4)_2$.

NOTES:

1.16 Wednesday, January 20, 2010, time: F. Reuter

Molecular magnetic units

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Here we present N,N,N',N'-Tetrakis-(pyridylmethyl)-benzene-1,4-diamine (TPBD) as a bridging ligand in different dinuclear homometallic transitionmetal complexes. The π-electron delocalisation of the bridging benzene-ring allows for a spin exchange between the two coordinated transition metal ions. Unfortunately however, the bridging mode leads to an antiferromagnetic spin exchange, from which a spin ground state of $S=0$ results. The task is therefore to modify the complex such that a high spin ground state results. There are at least two possible ways to reach this goal: By oxidizing the TPBD e.g. with I_2, it is transferred to its radical state and thus an additional paramagnetic centre arises in the system, leading to spin alignment of paramagnetic metal centres. The lifetime of such radical species strongly depend on the type of coordinating metal ions and also on used secondary ligands, necessary to complete the coordination sphere of the metal ion. The second possibility is to build up complexes consisting of metal ions with different spin quantum numbers. So, although antiferromagnetic coupling is dominating, the resulting spin ground state will be unequal zero. Structural, electrochemical and spectroscopic properties of homometallic dimeric complexes and their derivatives so far synthesised are presented herein.

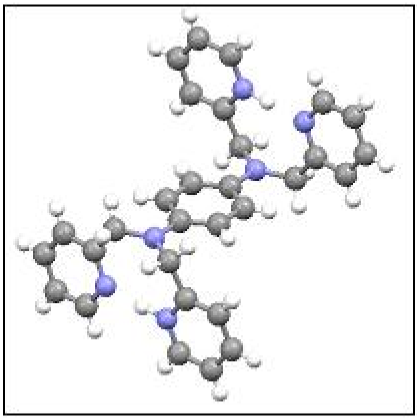

Figure 4: N,N,N',N'-Tetrakis-(pyridylmethyl)-benzene-1,4-diamine (TPBD).

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